First-principles calculations of hole trapping and transport: Effects on scintillator luminescence

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Abstract

An ab initio molecular orbital program is applied to clusters to compute energies and electron densities that describe the formation and transport of holes produced by ionizing radiation and their effects on luminescence of inorganic scintillator crystals. The resulting electron density plots for CsI show that a relaxed hole is shared equally by two bound I atoms (the classic V_k center). The calculated energy barrier for motion of the self-trapped hole is in excellent agreement with that expected from experimental measurements of the temperature dependence of the slow scintillation rise time of Tl-activated CsI. For CaF_2 initial V_k center formation is again predicted. The calculated energy barrier against hole migration is in reasonable agreement with the experimental value, however the scintillation rise time of Eu^{2+}-activated CaF_2 is very fast. In this case the Eu^{2+} activator promptly captures a hole before it can become self-trapped. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hole trapping; Hole transport; Scintillator luminescence; Cluster calculations

1. Introduction

The scintillation process in inorganic materials is commonly divided into the following steps: (1) the ionization event, that is, the production of dispersed holes and electrons that subsequently thermalize to the top of the valence band and the bottom of the conduction band, respectively (during this process the holes should be considered hot, meaning that no lattice relaxation has yet taken place), (2) energy transfer to and activation of the luminescent centers, and (3) radiative emission from the luminescent center. Steps 1 and 3 are relatively well understood [1]; here we focus on step 2. Because hole transport to activators is essential for efficient scintillation in many materials, the ability to model such processes computationally can be used to guide the search for improved scintillator materials.

2. Computational procedures

Calculations were performed using clusters of 15 or more atoms. It is important to allow for lattice relaxation, therefore the selection of cluster size and the number of atoms that are allowed to move must be tempered by consideration of the computational cost. An array of about 10 000 point charges was used to provide the electrostatic potential of the lattice in the region of the cluster atoms; the method for choosing point charges is described in detail in Ref. [2].

To compute energies and electron densities, the Schrödinger equation was solved at the Hartree–Fock (HF) level using the program Jaguar [3]. Standard basis sets with relativistic effective core potentials were used and diffuse functions were included. Möller–Plesset second-order (MP2) calculations provided electron correlation corrections to the energies (the importance of MP2 was established previously for NaCl [4]). For geometrical optimizations of the central atoms in the cluster, density functional theory (DFT) with an exact HF exchange functional and Perdew–Wang GCA-II (1991) local and non-local correlation functionals was employed. After the ground state HF-MP2 energy is calculated, the

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calculation is repeated with a cluster charge one higher than that of the ground state to represent the hole state and with a cluster charge one lower than the ground state to represent the excess electron state. Atomic charges were determined by direct integration of the charge density and were in qualitative agreement with those obtained from a natural population analysis.

The runs were performed on a Silicon Graphics, Inc. computer consisting of 12 R10 000 processors and on a Cray J-90 computer at the U.S. Department of Energy National Energy Research Supercomputer Center at the Lawrence Berkeley National Laboratory.

Two processes for activation of the luminescent center are of interest. One is when an activator ion first captures an electron and the holes self-trap (e.g., form V_k centers) followed by migration of a hole to the activator. In this case the scintillation rise time is limited by the transport barrier for hole diffusion. A second process is one wherein an activator captures the hot hole, before it can become self-trapped, followed by prompt electron capture. In this case the scintillation rise time will be fast. We can determine whether the activator prefers initial hole or electron capture by defining the following quantities $\Delta E_{h\text{-}g}(\text{undoped})$, $\Delta E_{e\text{-}g}(\text{undoped})$, $\Delta E_{h\text{-}g}(\text{doped})$, $\Delta E_{e\text{-}g}(\text{doped})$ which are the energy differences between the hole state and the ground state and the excess electron state and the ground state for undoped and doped material, respectively. We compare the energy differences $\Delta E_{h\text{-}g}(\text{undoped}) - \Delta E_{h\text{-}g}(\text{doped})$ and $\Delta E_{e\text{-}g}(\text{undoped}) - \Delta E_{e\text{-}g}(\text{doped})$; the quantity with the lower energy determines whether holes or electrons are initially trapped.

3. Results

3.1. Cesium Iodide

The above calculational approach was applied to CsI by considering a cluster of 32 Cs and 33 I atoms in an electrostatic field generated by 8192 point charges. The cluster was centered about an iodine atom; the seven central iodine and eight central cesium atoms were allowed to relax freely. The movable atoms are surrounded by a sufficient number of atoms to provide realistic interatomic forces. The relaxed CsI hole is found to be initially shared equally by two bound I atoms, a

classic V_k center. The barrier for the linear motion of the self-trapped hole was determined by exploring how a V_k center can be shifted between two pairs of I sites as the intervening I position is varied (the present cluster is sufficient to produce a V_k center on two symmetric sites). The calculated energy barrier for hole transport in CsI was found to be 0.23 eV [5]. This result is in excellent agreement with the activation energy for hole migration found from the temperature dependence of the scintillation rise time of thallium-activated CsI [6]. Thus the Tl^+ first captures an electron, followed by the delayed capture of a hole to form an excited luminescent center. (Note that the observed fast rise time associated to the excitonic emission in pure CsI [7] is not limited by the transport barrier because after the V_k center has formed, the V_k center rapidly captures an electron to form a self-trapped exciton (STE).)

3.2. Calcium Fluoride

In pure CaF_2 V_k centers are also formed and are preferentially aligned along the [0 0 1] direction. The energy barrier for migration was calculated using a cluster of 16 Ca and 32 F atoms. The resulting barrier, determined as described above, is 0.21 eV which is about 0.1 eV lower than the value determined by Beaumont et al. [8] by monitoring the motion of hole centers in $CaF_2 : Tm$ by EPR methods.

The observed scintillation rise time of Eu^{2+}-activated CaF_2, however, is < 30 ps [7]. This can occur by efficient hot hole capture by the Eu^{2+} activator (self-trapping of the hole and electron capture to form a STE is also possible) and is confirmed by a comparison of the energies for ground, hole, and excess electron states calculated for a simple cluster of 5 Ca and 10 F atoms using a non-local-density-approximation (BLYP) DFT simulation. A similar calculation shows that Tm^{3+} is expected to capture an electron. The results for Tm^{3+} and Eu^{2+} are summarized in Table 1. The predicted and observed behaviors are also consistent with the known stable divalent and trivalent valence states of these ions. The large difference in the rise times for the two activators can be understood as electron capture by Tm^{3+} followed by slow hole migration versus fast hot hole capture by Eu^{2+} followed by fast electron capture.

Table 1
Calculated energy comparisons and rise times for Tm^{3+}- and Eu^{2+}-activated Ca_5F_{10} clusters (relaxation energy is not included but is not expected to affect the conlusions)

Activator	$\Delta E_{h\text{-}g}(\text{doped}) - \Delta E_{h\text{-}g}(\text{undoped})$ (eV)	$\Delta E_{e\text{-}g}(\text{doped}) - \Delta E_{e\text{-}g}(\text{undoped})$ (eV)	Rise time
Tm^{3+}	0.0493	− 0.0307	∼ 1 µs (est.)
Eu^{2+}	− 0.619	− 0.053	< 30 ps [7]

4. Conclusions

For efficient, fast-rise-time-activated scintillators of the type considered here, hot hole capture by the activator should take place and dominate self-trapping. The present results show that computations can predict such behavior and therefore can provide guidance in the experimental search for new fast and efficient scintillator materials. The above methods are currently being applied to other scintillator materials including various pure and activated oxide (e.g., $ZnO : Ga$), halide (e.g., PbF_2), and chalcogenide (e.g., $Cds : Te$). Cerium-activated scintillators such as Lu_2SiO_5 and $Lu_3Al_5O_{12}$ are also of interest.

Acknowledgements

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